Critical Fluctuations and G^E-Models for Ternary Mixtures

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Phase equilibria in ternary mixtures have an immense importance in technological processes, like separation, extraction and particle formation. Several models were developed to describe the phase behavior of ternary systems. Based on the excess Gibbs-energy representation, all models are mean-field in essence, i.e., they neglect the effect of critical fluctuations on the thermodynamic behavior and, therefore, they give incorrect results near critical points.

Recently, Anisimov, Sengers and collaborators[1,2] have developed a crossover theory that incorporates the correct asymptotic critical behavior and crosses over to mean-field behavior. Moreover, they used their crossover theory to include the effect of critical fluctuations in prototypical classical equations (van der Waals equation for one-component [3], NRTL equation for binary liquid-liquid equilibria [4]). In this paper we discuss the extension of the Anisimov and Sengers crossover theory (ASXT) to ternary systems. In order to apply ASXT, a thermodynamic potential that is isomorphic with the one-component Helmholtz-energy is required. For that purpose, a Legendre transformation of the Gibbs-energy defines the grand-potential $\Omega(T,x_2,\mu_{13})$ which, after minor changes in variables, allows the description of the ternary systems. The discrepancy between independent variables of G^E $(T,\{x_i\})$ models and of the isomorphic thermodynamic potential $\Omega(T,x_2,\mu_{13})$ is solved in an iterative way. The procedure is applied to simple G^E models. Impurity effects in binary systems, phase behavior of solid-saturated solutions in mixtures of two solvents are discussed.

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